

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 423 101 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
26.01.2000 Bulletin 2000/04

(51) Int. Cl.⁷: **C07F 17/00**, **C08F 4/642**,
C08K 5/00, **C08L 23/10**

(21) Application number: **90870177.4**

(22) Date of filing: **09.10.1990**

(54) Catalyst for producing hemiisotactic polypropylene

Katalysator zur Herstellung von hemi-isotaktischem Polypropylen

Catalyseur pour produire du polypropylène hémi-isotactique

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(30) Priority: **10.10.1989 US 419221**

(43) Date of publication of application:
17.04.1991 Bulletin 1991/16

(60) Divisional application:
96112193.6 / 0 742 227

(73) Proprietor:
FINA TECHNOLOGY, INC.
Plano, Texas 75024 (US)

(72) Inventor: **Ewen, John A.**
Houston, Texas 77058 (US)

(74) Representative:
Leyder, Francis et al
c/o Fina Research S.A.
Dept. Brevets
Zone Industrielle C
7181 Seneffe (Feluy) (BE)

(56) References cited:
EP-A- 0 351 392 **EP-A- 0 387 690**
EP-A- 0 407 870

- **JOURNAL OF THE AMERICAN CHEMICAL SOCIETY**, vol. 110, 1988, pages 6255-6256, American Chemical Society; J.A. EWEN et al.: "Syndiospecific propylene polymerization with group 4 metallocenes"
- **MACROMOLECULES**, vol. 18, 1985, pages 928-932; G. DI SILVESTRO et al.: "Resolution of the carbon-13 nuclear magnetic resonance spectrum of hemiisotactic polypropylene at the decad and undecad level"

Remarks:

Divisional application 96112193.6 filed on 27/07/96.

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 423 101 B1

Description

BACKGROUND OF THE INVENTION

5 [0001] FIELD OF THE INVENTION: This invention relates, generally, to a catalyst system. Specifically, this invention relates to hemiispecific catalysts.

[0002] DESCRIPTION OF RELATED ART: Olefins, especially propylene, may be polymerized to form polyolefins in various forms: isotactic, syndiotactic and atactic. Isotactic polypropylene contains principally repeating units with identical configurations and only a few erratic, brief inversions in the chain. Isotactic polypropylene may be structurally represented in a Fischer projection as

(1)

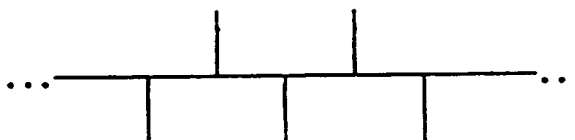


20 [0003] In Bovey's NMR nomenclature the isotactic structure is designated ...mmmm... since the five successive methyl groups are meso to each other, i.e., on the same side of the plane in a Fischer projection.

[0004] Isotactic polypropylene is capable of being a highly crystalline polymer with a high melting point and other desirable physical properties that are considerably different from the polymer in an amorphous (noncrystalline) state.

25 [0005] A syndiotactic polymer contains principally units of exactly alternating stereoisomers and is represented in a Fischer projection by the structure:

(2)

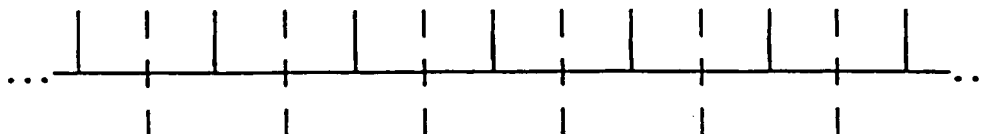


35 [0006] In Bovey's NMR nomenclature the syndiotactic structure is designated ...rrrr... since the five successive methyl groups are racemic to each other, i.e., on alternate sides of the plane in a Fischer projection.

40 [0007] A polymer chain showing no regular order of repeating unit configurations is an atactic polymer. In commercial applications, a certain percentage of atactic polymer is typically produced with the isotactic form.

[0008] There are other variations in the form of polymer structure. Hemiisotactic or hemitactic polypropylene was disclosed in "Hemitactic Polypropylene: An Example of a Novel Kind of Polymer Tacticity" by M. Farina, G. Di Silvestro and P. Sozzani (Macromolecules, Vol. 15, 1451-1452, 1982). The structure of hemiisotactic polymers is represented in a Fischer projection as follows:

(3)



55 [0009] The monomeric unit of the polymer is of the following structure:

(4)



where R_S is a hydrocarbonyl group or nonhydrocarbonyl group. The second carbon atom in formula (4) is the asymmetric carbon atom, i.e., the one which does not have identical groups attached, hence "asymmetric".

[0010] The structure of the polymer is characterized by R_S groups attached to every other asymmetric carbon atom being on the same side of the principal polymer chain as represented in a Fischer projection and R_S groups attached to the remaining asymmetric carbon atoms being either on the same side or the opposite side of the R_S groups attached to every other asymmetric carbon atom. When R_S groups are on the same side of the principal polymer chain, the structure is isotactic. Since only every other one conforms to the isotactic structure, it is "hemi". The material is a noncrystalline polymer.

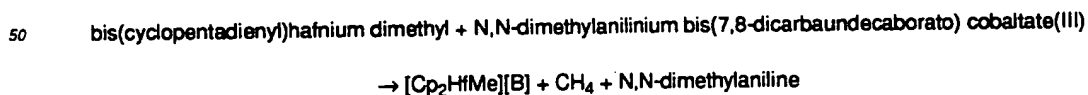
[0011] Polymerization of olefins is primarily with Ziegler-Natta catalysts. One family of Ziegler-Natta catalysts is Group IV metallocene compounds with methylaluminoxane as a cocatalyst. German patent application No. 2,608,863 discloses a catalyst system for the polymerization of ethylene consisting of bis(cyclopentadienyl)titanium dialkyl, an aluminum trialkyl and water. German patent application No. 2,608,933 discloses an ethylene polymerization catalyst system consisting of zirconium metallocenes of the general formula $(\text{cyclopentadienyl})_n\text{ZrY}_{4-n}$, wherein Y represents $R_1\text{CH}_2\text{AlR}_2$, $\text{CH}_2\text{CH}_2\text{AlR}_2$ and $\text{CH}_2\text{CH}(\text{AlR}_2)_2$ where R stands for an alkyl or metallo alkyl, and n is a number within the range 1-4; and the metallocene catalyst is used in combination with an aluminum trialkyl cocatalyst and water.

[0012] The use of metallocenes as catalysts in the copolymerization of ethylene and other alpha-olefins is also known in the art. U.S. Pat. No. 4,542,199 to Kaminsky, et al. discloses a process for the polymerization of olefins and particularly for the preparation of polyethylene and copolymers of polyethylene and other alpha-olefins. The disclosed catalyst system includes a catalyst of the formula $(\text{cyclopentadienyl})_2\text{MeRHal}$ in which R is a halogen, a cyclopentadienyl or a $\text{C}_1\text{-C}_6$ alkyl radical, Me is a transition metal, in particular zirconium, and Hal is a halogen, in particular chlorine. The catalyst system also includes an alumoxane having the general formula $\text{Al}_2\text{OR}_4(\text{Al}(\text{R})\text{-O})_n$ for a linear molecule and/or $(\text{Al}(\text{R})\text{-O})_{n+2}$ for a cyclic molecule in which n is a number from 4-20 and R is a methyl or ethyl radical. A similar catalyst system is disclosed in U.S. Pat. No. 4,404,344.

[0013] U.S. Pat. No. 4,530,914 discloses a catalyst system for the polymerization of ethylene to polyethylene having a broad molecular weight distribution and especially a bimodal or multimodal molecular weight distribution. The catalyst system is comprised of at least two different metallocenes and an alumoxane. The patent discloses metallocenes that may have a bridge between two cyclopentadienyl rings with the bridge serving to make those rings stereorigid.

[0014] European Patent Publication No. 0185918 discloses a stereorigid, chiral zirconium metallocene catalyst for the polymerization of olefins. The application does not indicate that hafnium could be substituted for the zirconium and used to produce a useful polymer product. The bridge between the cyclopentadienyl groups is disclosed as being a linear hydrocarbon with 1-4 carbon atoms or a cyclical hydrocarbon with 3-6 carbon atoms.

[0015] European Patent Application 0-277-003 relates to work by Turner on a catalyst prepared by a protonation method. A bis(cyclopentadienyl) metal compound is combined with a compound having a cation capable of donating a proton and an anion having a plurality of boron atoms. For example, the following reaction illustrates the invention:



where [B] is 7,8-dicarbaundecaborane.

[0016] European Patent Application 0-277-004 also relates to work by Turner on a catalyst prepared by a protonation method. A bis(cyclopentadienyl) metal compound is combined with an ionic compound having a cation which will irreversibly react with a ligand on the metal compound and an anion having a plurality of lipophilic radicals around a metal or metalloid ion. For example, the following reaction illustrates the invention:

tri(n-butyl)ammonium tetra(pentafluorophenyl)boron + bis(cyclopentadienyl) zirconium dimethyl

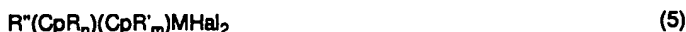


[0017] Syndiospecific propylene polymerization with an isopropyl(cyclopentadienyl-1-fluorenyl)hafnium dichloride metallocene catalyst yielding crystalline polymer in high yields is disclosed in "Syndiospecific Propylene Polymerizations with Group 4 Metallocenes", J. Am. Chem. Soc., Vol. 110, pp. 6255-6256, 1988.

[0018] A system for the production of isotactic polypropylene using a titanium or zirconium metallocene catalyst and an alumoxane cocatalyst is described in "Mechanisms of Stereochemical Control in Propylene Polymerization with Soluble Group 4B Metallocene/Methylalumoxane Catalysts," J. Am. Chem. Soc., Vol. 106, pp. 6355-64, 1984. The article shows that chiral catalysts derived from the racemic enantiomers of ethylene-bridged indenyl derivatives form isotactic polypropylene by the conventional structure predicted by an enantiomorphic-site stereochemical control model. The meso achiral form of the ethylene-bridged titanium indenyl diastereomers and achiral zirconocene derivatives, however, produce polypropylene with a purely atactic structure.

SUMMARY OF THE INVENTION

[0019] In accordance with the present invention, there is provided a metallocene compound having a general formula of



where Cp of CpR_n is cyclopentadienyl and Cp of CpR'_m is fluorenyl, each R and R' is a hydrocarbyl radical having from 1-20 carbon atoms, is the same or different and is selected such that CpR'_m is a sterically different ring from CpR_n resulting in a lack of bi-lateral symmetry for the compound, R'' is a structural bridge (cf. claim 1) imparting stereorigidity to the compound, M is a Group 4 metal, n is from 1 to 4, m is from 0 to 4 and Hal is a halogen. One example of such a compound is isopropylidene (3-methylcyclopentadienyl-1-fluorenyl) zirconium dichloride. This compound is a bridged, metallocene compound having dissimilar cyclopentadienyl groups and no bi-lateral symmetry.

[0020] One use for these compounds is in a metallocene catalyst system. The metallocene compounds defined above can be activated as catalysts by any known method of metallocene catalyst preparation.

[0021] The metallocene catalyst comprises:

- (a) a metallocene compound; and
- (b) an ionizing agent;

wherein the metallocene compound comprises the general formula:

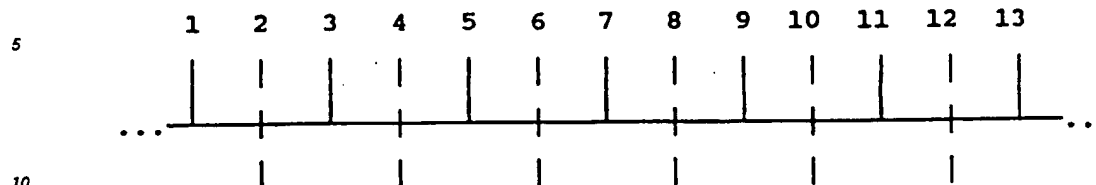


wherein Cp of CpR_n is cyclopentadienyl and Cp of CpR'_m is fluorenyl, each R and R' is a hydrocarbyl radical having from 1-20 carbon atoms and is the same or different and is selected such that CpR'_m is a sterically different ring from CpR_n resulting in a lack of bi-lateral symmetry for the compound, R'' is a structural bridge imparting stereorigidity to the compound, M is a Group 4 metal, n is from 1 to 4, m is from 0 to 4 and Hal is a halogen.

[0022] The polymer produced with the catalyst of this invention has the structure termed "hemiisotactic". Hemiisotactic polypropylene is characterized by every other methyl group being on the same side of the principal polymer chain as represented by a Fischer projection. The remaining methyl groups can be either on the same side or the opposite side of the principal polymer chain.

[0023] Propagation of the polymer chain results from head-to-tail linkage of the propylene monomer units in such a way the following structure is formed:

(6)



[0024] In this Fischer projection representation the odd numbered methine units are meso with respect to each other and the even numbered methine carbons have random steric configurations. Hemiisotactic polypropylene is noncrystalline due to the disorder and irregularity of these random groups.

DESCRIPTION OF THE INVENTION

[0025] The invention is for a new metallocene compound which is a catalyst precursor for a catalyst used to produce polymers termed hemiisotactic. The metallocene compound is changed to a metallocene catalyst with an ionizing agent which converts the neutral metallocene compound to a metallocene cation which operates as a catalyst. The ionizing agent can be a cocatalyst compound such as methylaluminoxane (MAO).

[0026] A preferred application of the invention is in the hemiisotactic polymerization of monomers which may be characterized in terms of the following formula:



wherein R_g is a hydrocarbyl group or nonhydrocarbyl substituent. Monomers to which the present invention is applicable are C_3+ alpha olefins, 1-butene, 1-dienes, such as 1,3-butadiene, substituted vinyl compounds, such as vinyl chloride, and styrene. The preferred application is to ethenically unsaturated monomers. By the term "ethenically unsaturated monomer" as used herein is meant a hydrocarbon or substituted hydrocarbon compound characterized by a terminal vinyl group ($\text{CH}_2=\text{CH}-$). The most preferred ethenically unsaturated compounds employed in the present invention have at least three carbon atoms. A specific example is propylene.

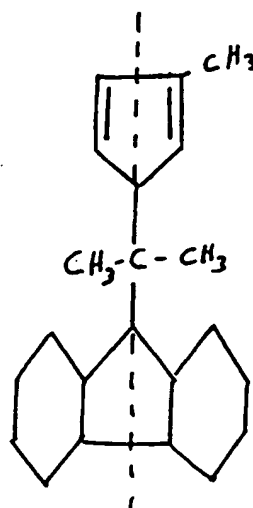
[0027] The catalyst used to produce hemiisotactic olefins is from a metallocene compound having a general formula of



as defined above.

[0028] The lack of bi-lateral symmetry for the compound is defined as the condition in which a metallocene compound having one non-cyclopentadienyl coordination site has no substituents or one or more substituents on one side of the cyclopentadienyl rings both above and below the coordination site and one or more substituents on the other side of the cyclopentadienyl rings either above or below the coordination site. One example of such a compound is isopropylidene(3-methylcyclopentadienyl-1-fluorenyl)zirconium dichloride, abbreviated $\text{iPr}(\text{3MeCp-1-Flu})\text{ZrCl}_2$. An illustration of the ligand of this compound is shown below:

(9)



[0029] The lack of bi-lateral symmetry is illustrated by the right side of the drawing being different from the left because one methyl group is on the right side of one cyclopentadienyl ring and no substituents are on the left side of the same cyclopentadienyl ring.

[0030] The $\text{iPr}(\text{3MeCp-1-Flu})\text{ZrCl}_2$ compound was prepared by cracking the methylcyclopentadiene dimer, preparing 3,6,6-trimethylfulvene, bridging the two cyclopentadiene compounds with an isopropylidene bridge and forming a coordination compound with zirconium and chlorine. Final reactions were carried out in tetrahydrofuran (THF) and in methylenedichloride (MeCl_2), also known as dichloromethane. Use of MeCl_2 allows the $\text{iPr}(\text{3MeCp-1-Flu})\text{ZrCl}_2$ to be isolated in pure form.

[0031] Polymerization of the olefin is accomplished by any of the known means for polymerization of olefins with metallocene catalysts, for example polymerization in bulk, slurry or gas phase. For polypropylene, polymerization temperatures range from -80°C to 150°C , preferably 25°C to 90°C and most preferably from 50°C to 80°C .

[0032] The noncrystalline hemiisotactic polypropylene has use as a plasticizer for syndiotactic or isotactic polypropylene. A plasticizer is a material incorporated in a plastic to increase its workability and its flexibility or distensibility. The addition of a plasticizer may lower the melt viscosity, the temperature of the second-order transition, or the elastic modulus of the plastic. The plastic and plasticizer are intimately mixed which is most commonly done by heating until the plastic has dissolved into the plasticizer or vice versa. Alternatively, the plastic and plasticizer are mixed by dissolution in a common solvent without heat followed by removal of the solvent by evaporation.

[0033] Hemiisotactic polymer is noncrystalline and with its partial stereoregular structure would have properties of a plasticizer. A specific example of a hemiisotactic polymer as a plasticizer is a reactor blend of hemiisotactic polypropylene and syndiotactic polypropylene made by polymerizing propylene simultaneously with both $\text{iPr}(\text{3MeCp-1-Flu})\text{ZrCl}_2$ and isopropylidene (cyclopentadienyl -1-fluorenyl)zirconium dichloride, abbreviated $\text{iPr}(\text{Cp-1-Flu})\text{ZrCl}_2$, or any other syndiospecific catalyst precursor. A reactor blend of hemiisotactic and isotactic polypropylene is possible by polymerizing propylene simultaneously with both $\text{iPr}(\text{3MeCp-1-Flu})\text{ZrCl}_2$ and ethylenebis(tetrahydroindenyl)zirconium dichloride, abbreviated $\text{Et}(\text{IndH}_4)_2\text{ZrCl}_2$, or any other isospecific catalyst precursor. The amount of hemiisotactic polypropylene in mixture with isotactic or syndiotactic polypropylene can range from 1-90% by weight, depending on desired physical properties of the plasticized plastic. Preferably, the amount of hemiisotactic polypropylene in mixture with isotactic or syndiotactic polypropylene ranges from 5-50 % by weight. Most preferably, the amount of hemiisotactic polypropylene in mixture with isotactic or syndiotactic polypropylene is approximately 10% by weight.

[0034] The invention having been generally described, the following examples are given as particular embodiments of the invention and to demonstrate the practice and advantages thereof.

EXAMPLE I

A. Preparation of 3,6,6-trimethylfulvene

[0035] 150 ml of methylcyclopentadiene dimer was fractionally distilled from 100 ml of mineral oil and at 62°C and collected at 0°C. 500 mmol of methyl lithium (1.4M; diethylether) were added, dropwise, to a mixture of 500 mmol of freshly distilled methylcyclopentadiene and 137 ml of dry acetone at 0°C. The solution was stirred for 1 hour at 25°C. 8g (85% yield) of 3,6,6-trimethylfulvene were recovered from the organic layer by vacuum distillation after an extraction with 100 ml of saturated, aqueous NH_4Cl and drying over MgSO_4 .

B. Preparation of $\text{iPr}(3\text{-MeCp-1-Flu})$

[0036] One mole of 3,6,6-trimethylfulvene was dissolved in 100 ml THF and added, dropwise, to cold (-78°C) solution containing 1 mol of the lithium salt of the fluorenyl anion in approximately 100 ml THF and 714 ml of diethyl ether. The mixture was warmed to room temperature. 18 g of white powder were obtained from the organic layer as a single isomer by extracting with aqueous NH_4Cl , drying over MgSO_4 , filtering concentrating under vacuum to an oil, dissolving in chloroform, precipitating and washing with excess methanol. ^1H NMR CD_2Cl_2 , int. ref. Me_4Si $\delta = 0$ ppm: 7.7d, 7.3t, 7.2d and 7.1t (8) (Flu C6 rings); 6.5t and 5.6d (2) (Cp vinyl); 4.1s (1) (Flu C5 ring methine); 2.95s (2) (Cp methylene); 2.2d (3) (Cp methyl); 1.0s (6) (isopropyl methyl). (1 stereoisomer: The Cp methylene signal appears as a singlet because the methylene group is alpha to both the iPr bridge and the Cp methyl).

C1. Preparation of isopropylidene(3-methylcyclopentadienyl-1-fluorenyl)zirconium dichloride in methylene chloride.

[0037] 2 equivalents of methyl lithium (1.4 M in diethylether) were added, dropwise, at -78°C to 5 g of isopropylidene (3-methylcyclopentadiene-1-fluorene) dissolved in 100 ml THF, warmed to 25°C, and stirred for 12 hours. The red dilithio salt was isolated by evaporating the solvents under vacuum and then purified by washing with two 150 ml portions of dry, deoxygenated pentane that were cannulated away in term. The dianion was dissolved in methylene chloride at -78°C and an equivalent of ZrCl_4 , slurried in 125 ml CH_2Cl_2 at -78°C, was rapidly cannulated into the flask containing the soluble dianion. The stirred mixture was warmed slowly to 25°C and stirred for 12 hours. A white solid was filtered off. 3 g of a moderately air sensitive, orange powder were obtained by concentrating the methylene chloride under vacuum, cooling the -20°C for 12 hours and cannulating the supernatant away. The product was purified by recrystallizing it from methylene chloride. $\text{ZrCl}_2\text{C}_{22}\text{H}_{20}$ requires C, 59; H, 4.5. Found: C, 56; H, 4.4. ^1H NMR (δ , ppm) CD_2Cl_2 , int. ref. TMS $\delta = 0$ ppm: 8.15-8.10 2d (2), 7.87-7.78 2d (2), 7.55-7.48 2t (2), 7.27-7.21 m (2) (Flu C6 rings); 5.93 t (1), 5.63 t (1), 5.42 t (1) (Cp vinyl); 2.4 d (6) (isopropyl methyl); 2.0 s (3) (Cp methyl).

C2. Preparation of isopropylidene(3-methylcyclopentadiene-1-fluorenyl)zirconium dichloride in THF

[0038] 34 mmol methyl lithium in diethyl ether (1.4M) were added, dropwise, at 25°C, with stirring, to 5 gms of $\text{iPr}[3\text{-methylcyclopentadienyl-1-fluorene}]$ ligand, then dissolved in 75 cc's THF which was contained in a round bottom flask equipped with a sidearm and dropping funnel. The dark orange/red solution was stirred for several hours after gas evolution had ceased. 6.41 gms of $\text{ZrCl}_4 \cdot 2 \text{ THF}$ were dissolved in 100 ml of THF at 40°C. The dianion was cannulated into the flask containing the $\text{ZrCl}_4 \cdot 2 \text{ THF}$ at 25°C. The mixture was stirred for 18 hours. The solution was then cannulated into a flask and cooled to -20°C to obtain a crystalline product. Alternatively, the THF was evaporated under vacuum. 5 mg of the $\text{LiCl/iPr}[3\text{MeCp-1-Flu}]\text{ZrCl}_2$ mixture was added to MAO for a polymerization test.

EXAMPLE II

[0039] 1.4 cc of methylaluminoxane (MAO) were mixed with 5 mg of $\text{iPr}(3\text{MeCp-1-Flu})\text{ZrCl}_2$ prepared in THF as in Example I and dissolved in 10-20 ml of toluene. The MAO was 37 weight percent (Scherring). 1.2 liter of propylene was added to the reactor. The mixture was stirred for 10 minutes. Reactor temperature was set at 60°C.

[0040] The catalyst solution was added to a 50 ml stainless steel bomb. 200 ml of propylene was pumped through the bomb into the reactor. The contents of the reactor were agitated for 60 minutes.

[0041] The reaction product was dried in a vacuum. The polymer was weighed and analyzed for molecular weight distribution. The results are shown in Table I.

EXAMPLE III

[0042] The procedure of Example II was repeated using 1.4 cc of MAO, 1.2 l of propylene, 5 mg of $\text{iPr}(3\text{MeCp-1-Flu})\text{ZrCl}_2$.

Flu)ZrCl₂, a reaction temperature of 30°C and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE IV

5 [0043] The procedure of Example II was repeated using 1.4 cc of MAO, 1.2 l of propylene, 5 mg of iPr(3MeCp-I-Flu)ZrCl₂ prepared in MeCl₂ as in Example I, a reactor temperature of 65°C and a run time of 60 minutes. The results are shown in Table I.

10 [0044] A C-13 NMR spectra was obtained for the polymer from this run. The probability of the occurrence of a particular sequence of meso and racemic polymer structures for hemiisotactic polypropylene was calculated based on the method in "Hemitactic Polypropylene: An Example of a Novel Kind of Polymer Tacticity". The results for the calculated versus the observed values as a function of the relative intensity of the NMR spectra are shown in Table II.

EXAMPLE V

15 [0045] 5.0 cc of MAO were mixed with 5 mg of iPr(3MeCp-I-Flu)ZrCl₂ prepared in MeCl₂ as in Example I above and dissolved in 10-20 ml of toluene. The MAO was 10 weight percent (Scherring). 1.4 l of propylene was added to the reactor. The mixture was stirred for 10 minutes. Reactor temperature was set to 60°C.

20 [0046] 0.4 mg of isopropylidene(cyclopentadienyl)-1-fluorenyl)zirconium dichloride, abbreviated iPr(Cp-I-Flu)ZrCl₂, was dissolved separately in 10-20 ml of toluene. The two catalyst solutions were mixed together and added to a 50 ml stainless steel bomb. 200 ml of propylene was pumped through the bomb into the reactor. The contents of the reactor were agitated for sixty minutes.

[0047] The reaction product was dried in a vacuum. The polymer was weighed and analyzed for melting point. The results are shown in Table I.

25 [0048] All general synthetic procedures were performed under an inert atmosphere using a Vacuum Atmospheres glovebox or Schlenk techniques. Toluene, pentane and tetrahydrofuran solvents were distilled under nitrogen from purple sodium/benzophenone-ketyl. Dichloromethane was distilled from fresh calcium hydride under nitrogen.

[0049] The following results are from the experimental runs described above using the method of the present invention.

TABLE I

Example	Metallocene Compound mg	MAO cc's	Propylene l	T, °C
	iPr(3MeCp-I-Flu)ZrCl ₂			
2	5	1.4	1.2	60
3	5	1.4	1.2	30
4	5	1.4	1.2	65
	iPr(3MeCp-I-Flu)ZrCl ₂ /iPr(Cp-I-Flu)ZrCl ₂			
5	5/0.4	5.0	1.4	60
Example	t, min.	Yield g	M _w /M _n	
2	60	184	1.9	
3	60	32		
4	60	297	3.4	
5	60	162		

TABLE II

Sequence	Calculated	Observed
mmmm	0.15	0.14
mmmr	0.11	0.12
rmmr	0.07	0.06
mmrr	0.25	0.21
xmrx	0.00	0.05
mrmr	0.00	0.00
rrr	0.23	0.19
rrrm	0.14	0.14
mrrm	0.06	0.08

[0050] This invention has taken a known syndiospecific catalyst precursor with bi-lateral symmetry and added a methyl group on one of the cyclopentadienyl groups to eliminate the bi-lateral symmetry. The new catalyst produces a structure of polypropylene termed hemiisotactic due to every other methyl group of the polypropylene being above the plane in a Fischer projection. Hemiisotactic polypropylene is noncrystalline and can be used as a plasticizer with syndiotactic and isotactic polypropylene.

Claims

1. A metallocene compound comprising the general formula:



where Cp of CpR_n is cyclopentadienyl and Cp of CpR'_m is fluorenyl, each R and R' is a hydrocarbyl radical having from 1-20 carbon atoms and is the same or different and is selected such that CpR' is a sterically different ring from CpR_n resulting in a lack of bi-lateral symmetry for the compound, R'' is a structural bridge imparting stereoridity to the compound and connecting the cyclopentadienyl moieties with each other, M is a Group 4 metal, n is from 1 to 4, m is from 0 to 4 and Hal is a halogen.

2. A metallocene compound as recited in claim 1 wherein M is titanium, zirconium and hafnium.
3. A metallocene compound as recited in claim 1 wherein Hal is chlorine.
4. A metallocene compound as recited in claim 1 wherein the compound is isopropylidene (3-methylcyclopentadienyl-1-fluorenyl) zirconium dichloride.
5. A metallocene catalyst comprising:

a) a metallocene compound; and

b) an ionizing agent;

wherein the metallocene compound comprises the general formula:



wherein Cp of CpR_n is cyclopentadienyl and Cp of CpR'_m is fluorenyl, each R and R' is a hydrocarbyl radical having from 1-20 carbon atoms and is the same or different and is selected such that CpR' is a sterically different ring from CpR_n resulting in a lack of bi-lateral symmetry for the compound, R'' is a structural bridge imparting stereoridity to the compound and connecting the cyclopentadienyl moieties with each other, M is a Group 4 metal, n is from 1 to 4, m is from 0 to 4 and Hal is a halogen.

6. A metallocene catalyst as recited in claim 5 wherein M is selected from the group consisting of titanium, zirconium and hafnium.
7. A metallocene catalyst as recited in claim 5 wherein Hal is chlorine.
8. A metallocene catalyst as recited in claim 5 wherein the compound is isopropylidene (3-methylcyclopentadienyl-1-fluorenyl) zirconium dichloride.

Patentansprüche

1. Metallocenverbindung, umfassend die allgemeine Formel:



wobei C_p von C_pR_n Cyclopentadienyl ist, und C_p von $C_pR'_m$ Fluorenyl ist, jedes R und R' ist ein Hydrocarbylrest mit 1 bis 20 Kohlenstoffatomen und ist das Gleiche oder unterschiedlich und ist so ausgewählt, daß C_pR' ein sterisch unterschiedlicher Ring von C_pR_n ist, was zu einem Fehlen an bilateraler Symmetrie für die Verbindung führt, R'' ist eine Strukturbrücke, die der Verbindung Stereorigidität verleiht und die Cyclopentadienylreste mit jedem anderen verbindet, M ist ein Gruppe 4 Metall, n ist von 1 bis 4, m ist von 0 bis 4, und Hal ist ein Halogen.

2. Metallocenverbindung nach Anspruch 1, wobei M Titan, Zirkonium und Hafnium ist.
3. Metallocenverbindung nach Anspruch 1, wobei Hal Chlor ist.
4. Metallocenverbindung nach Anspruch 1, wobei die Verbindung Isopropyliden (3-methylcyclopentadienyl-1-fluorenyl)zirkoniumdichlorid ist.
5. Metallocenkatalysator, umfassend:

- a) eine Metallocenverbindung und
 - b) ein Ionisierungsmittel,
- wobei die Metallocenverbindung die allgemeine Formel umfaßt:



wobei C_p von C_pR_n Cyclopentadienyl ist, und C_p von $C_pR'_m$ Fluorenyl ist, jedes R und R' ein Hydrocarbylrest mit 1-20 Kohlenstoffatomen ist und gleich oder unterschiedlich ist und so ausgewählt ist, daß C_pR' ein sterisch unterschiedlicher Ring von C_pR_n ist, was zu einem Mangel an bilateraler Symmetrie für die Verbindung führt, R'' ist eine Strukturbrücke, die der Verbindung Stereorigidität verleiht und die Cyclopentadienylreste miteinander verbindet, M ist ein Gruppe 4 Metall, n ist von 1 bis 4, m ist von 0 bis 4, und Hal ist ein Halogen.

6. Metallocenkatalysator nach Anspruch 5, wobei M aus der Gruppe bestehend aus Titan, Zirkonium und Hafnium ausgewählt ist.
7. Metallocenkatalysator nach Anspruch 5, wobei Hal Chlor ist.
8. Metallocenkatalysator nach Anspruch 5, wobei die Verbindung Isopropyliden (3-Methylcyclopentadienyl-1-fluorenyl)zirkoniumdichlorid ist.

Revendications

1. Un composé de métallocène ayant la formule générale:



où le Cp de CpR_n est du cyclopentadiényle et le Cp de CpR'_m est un fluorényle, chacun des R et R' est un radical hydrocarbyle ayant de 1 à 20 atomes de carbone et est le même ou différent et est choisi de telle façon que CpR' est un anneau stériquement différent de CpR_n ce qui résulte en une absence de symétrie bilatérale pour le com-

posé, R" est un pont structural communiquant une stéréorigidité au composé et raccordant les groupements cyclopentadiényles l'un à l'autre, M est un métal du groupe 4, n est entre 1 à 4, m est entre 0 à 4 et Hal est un halogène.

2. Un composé de métallocène selon la revendication 1 où M est le titane, le zirconium et le hafnium.
3. Un composé de métallocène selon la revendication 1 où Hal est le chlore.
4. Un composé de métallocène selon la revendication 1 où le composé est le dichlorure de isopropylidène (3-méthylcyclopentadiényl-1-fluorényl) zirconium.
5. Un catalyseur de métallocène comprenant:
 - a) un composé de métallocène; et
 - b) un agent ionisant;
 où le composé de métallocène comprend la formule générale:



ou le Cp de CpR_n est du cyclopentadiényle et le Cp de CpR'_m est du fluorényle, chacun des R et R' est un radical hydrocarbyle ayant de 1 à 20 atomes de carbone et est le même ou différent et est choisi de telle façon que CpR' est un anneau stériquement différent de CpR_n , ce qui résulte en une absence de symétrie bilatérale pour le composé, R" est un pont structural communiquant une stéréorigidité au composé et raccordant les groupements cyclopentadiényles l'un à l'autre, M est un métal du groupe 4, n est entre 1 à 4, m est entre 0 à 4 et Hal est un halogène.

6. Un catalyseur de métallocène selon la revendication 5 où M est choisi dans le groupe consistant en titane, zirconium et hafnium.
7. Un catalyseur de métallocène selon la revendication 5 où Hal est le chlore.
8. Un catalyseur de métallocène selon la revendication 5 où le composé est le dichlorure de isopropylidène(3-méthylcyclopentadiényl-1-fluorényl) zirconium.